1950

A comparison of methods of measuring the thicknesses of thin metal films

Van William Bearinger
Iowa State College

NOTE TO USERS

A COMPARISON OF METHODS OF MEASURING THE THICKNESSES OF THIN METAL FILMS

by

Van William Bearinger

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1950

TABLE OF CONTENTS

INTRODUCTION

The first relatively important publication on thin metal films by Faraday in 1857 opened a new field of investigation.[1] Since then a large number of experiments have been conducted to determine the physical properties of such films. The optical, electrical and magnetic properties have most frequently come under investigation.

Films 10 to 10,000 angstroms thick lend themselves well to most experimental determinations. These thicknesses, although greater than atomic dimensions, are still small enough so that properties of the films are different from those of the bulk metal. Therefore, it has been hoped that some interesting conclusions as to the structure of atoms and their arrangements in solids could be drawn from thin film research.

Of the physical constants determined, most has been done in the field of optics. The optical constants most commonly determined are the reflectance, transmittance, index of refraction and absorption coefficients. Several methods used to obtain these constants necessitate an accurate determination of the optical thicknesses of the

---

[1] P. A. Aron, Ann. Phys. Paris 1, 361 (1946).

semitransparent films[2], [3] because of the variation of electrical conductivity with film thickness.[4] In most cases the area density was determined and the film thicknesses calculated from the bulk density of the metal. Goos[2] used this method in his work and describes in much detail the techniques used.

In such a method it is necessary to weigh small quantities of deposited metal very accurately. It is also assumed that the density of the metal, when present in a very thin film, is the same as that of the bulk metal. The validity of this assumption is questionable. Road[5] found that the density of MgF_2 films 1000 A. U. thick is more than 10 percent less than that of the massive MgF_2. Electron microphotographs by Picard and Duffenback[6] show all the films studied to consist of aggregates of the metal separated by interstices of various widths. From this evidence, it is

---

[2] F. Goos, Zeits. f. Physik. 100, 95 (1936).

[3] M. S. Oldham, Ph. D. thesis, Department of Physics, I. S. C. (1949).

[4] R. Weale, Proc. Phys. Soc. 62, 576 (1949).

[5] J. L. Road, J. Opt. Soc. Am. 39, 854 (1949).

[6] R. G. Picard and O. S. Duffenback, J. App. Phys. 14, 291 (1943).

doubtful whether the thickness determined by weighing is the optical thickness required in the determination of the optical constants.

Oldham[3] determined the optical thickness interferometrically using a multiple-beam interference technique suggested by Tolansky.[7] This method does not require the density to be known, but instead, measures the difference in the optical distance between two light reflecting planes DE and EF, figure 1, from a reference reflecting plane BC. This difference is the apparent optical thickness of film G. A must be transparent to the incident, monochromatic light which arrives normal to surface BC. BC is a partially reflecting deposit which transmits about 5 percent of the incident light. The surface DEF has maximum reflectivity so that reflection interference fringes of the Fizeau type are produced between the surfaces BC and DEF.[8-10] The plate H can be either opaque or transparent. The surfaces of A and H must be optically plane to within 1/200 of the wave length of the incident light over a small local area including the discontinuity at E.

---

[7] S. Tolansky, J. Sci. Inst. 22, 161 (1945).

[8] S. Tolansky, Phil. Mag. 35, 120 (1944).

[9] S. Tolansky, Proc. Roy. Soc. 184, 41 (1945).

[10] S. Tolansky, Proc. Roy. Soc. 186, 261 (1946).

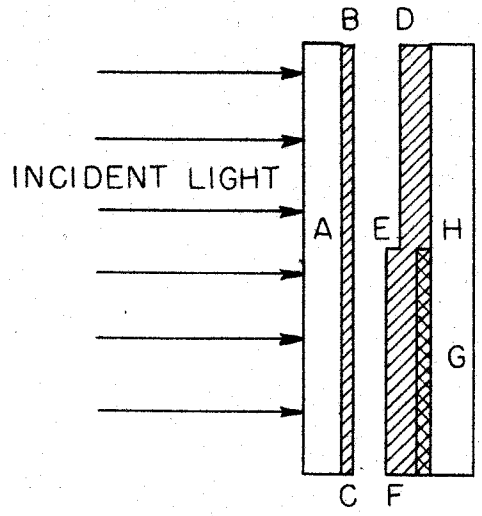

Fig. 1 Arrangement of interference surfaces.

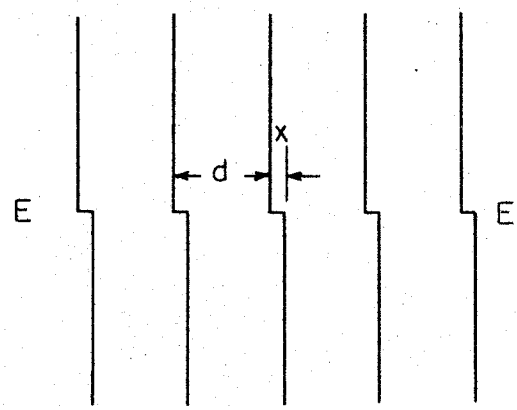

Fig. 2 Diagram of interference pattern.

If the inclination of surface BC to surface DEF is adjusted so that the interference fringes cross the discontinuity E at right angles to the line of the step, then a set of parallel fringes with a shift coincident with the line of the step is obtained. Such a set of fringes is shown diagrammatically in figure 2. The thickness S of film G can be calculated from the following formula:

$$S = \frac{\text{fringe shift } x}{\text{fringe separation } d} \times \frac{\text{Wave length of incident light}}{2}. \quad (1)$$

The factor of 1/2 occurs because the optical path difference is twice the height of the step.

Techniques for particle size determinations described by Williams and Backus[11] provide still another method of determining the thicknesses of evaporated films. By shadow-casting a heavy metal such as gold over a film edge, it is possible to determine the height of the edge by measuring the length of the shadow. Since the angle of incidence can be such as to produce shadows five to ten times the film height, thicknesses of 100 A. U. or less can be determined to within 10 A. U. Oldham[3] suggested this as a possible method, but did not develop the technique to the point of usefulness in his

---

[11] R. C. Williams and R. C. Backhus, J. App. Phys. 20, 98 (1949).

work. This method has been further developed by the author and is described later.

Still another method of film thickness determination used by Friedman[12] measures the amount of absorption of hard x-rays when passed through the film twice. This is done by reflecting the x-rays at a Bragg angle from the crystal lattice of the base material and comparing the intensity of the beam reflected from the coated section with that from the uncoated section. The intensities may be measured with a Geiger tube. It is necessary to know the absorption coefficient of the film for the wave length of x-rays used. This coefficient is known for bulk metals but not for the evaporated films of the metals. Therefore, the measurements are not absolute since the absorption coefficient of the bulk metal is used. The limit of accuracy of this method is well over 100 A. U. Consequently, it is not applicable to the measurement of films less than 1000 A. U. thick.

Of the four methods of measuring thicknesses described in the preceding paragraphs, the weighing method has been historically the most popular until the recent introduction of the interferometric method. As has already been pointed out, weighing fails to measure the absolute thickness since

---

[12] H. Friedman, Rev. Sci. Inst. 17, 99 (1946).

a bulk density is assumed for the metal in the form of a thin film. Only the interferometric and the electron microscope methods appear to give absolute thickness measurements.

A direct comparison of the three methods has not been reported in the literature. An indirect comparison of the interferometric measurements with the weighing measurements was performed by Oldham.[3] He assumed that the two gold films evaporated on quartz must have equal thickness if the transmittance of the two is the same. Oldham then compared the film thickness he had measured for a given transmittance with that measured by Goos[13] for the same transmittance. His measurements of thickness were by interferometry while Goos' were by weight. Oldham found that the thickness measurements by weight were in some cases as much as 50 percent less than those measured by the interferometer. These results must be qualified by the findings of Sennett and Scott[14] in which they found that the rate of deposition affects the structure and optical properties of metal films. The slow rates in general gave more aggregated structure and increased light absorption. Therefore, unless the films were deposited under exactly the same conditions, it is not

---

[13] F. Goos, Zeits. f. Physik. 106, 606 (1937).

[14] R. S. Sennett and G. D. Scott, J. Opt. Soc. Am. 40, 203 (1950).

safe to assume they have exactly the same optical properties.

Khamsavi and Donaldson[15] measured the density of silver films from 122 A. U. to 735 A. U. thick. They used a calorimetric determination of the mass deposited upon a given area and an interferometric determination of the thickness. They found, within experimental error, the density to be constant and the same as that of bulk silver. This constitutes a direct comparison and complete agreement between the weighing and interferometric methods. These results must be reconsidered after the findings of Avery.[16] He measured the thickness of the same film edge by depositing over one half of the sample an opaque reflecting layer DEF, figure 1, of chromium and over the other half a coating of silver. The support H, figure 1, was glass silver-coated to about 1000 A.U. for one set of data, but not coated for the other set. He found that for a substrate of silver the metal step measured 21 to 26 percent less for a silver coating DEF than for a chromium coating. In the case of a glass substrate the difference was 34 to 38 percent. The silver coating again indicated a smaller step. Percentage

---

[15]A. Khamsavi and W. K. Donaldson, Nature 159, 228 (1947).

[16]D. G. Avery, Nature 163, 916 (1949).

wise, the difference remained nearly constant for a given substrate, being greater for glass than for silver. These results indicate a "packing in" effect of the opaque reflecting layer DEF when deposited on the metal film sample G and substrate. This effect is greater for silver on silver than for chromium on silver. It must also depend upon the thickness of the film on which the metal is deposited since the difference is present even when the substrate and the film being measured are of the same metal. This "packing in" effect leads to a thinner apparent thickness and can account for the constant bulk density of the silver films measured by Khamsavi and Donaldson.

The preceding examples are cited to familiarize the reader with the problems involved in measuring the thicknesses of very thin metal films as well as the pitfalls into which one can stumble if the proper precautions are not taken. They also establish the need for further investigation leading to new techniques along with the improvement of those existing. This is the purpose of the present investigation.

The general plan of investigation can be divided into three parts: (1) to apply the shadow-casting technique of electron microscopy to the measurement of thin film thickness; this to be developed to a reasonable degree of accuracy, dependability and usability, (2) to directly compare

this method with the interferometric method by measuring the same film samples by both methods, and (3) to directly compare the weighing method with the interferometric method by measuring the same sample both ways. The weighing of very thin samples is to be eliminated by the introduction of a radioactive tracer method described in the next section.

EXPERIMENTAL METHODS

The general procedure for this investigation can be divided into four operations: (1) preparation of films, (2) determination of film thickness by the shadow-casting method, (3) determination of film thickness by the interferometric method, and (4) determination of film thickness by the radioactive tracer method. The techniques by which each of these operations was accomplished are discussed separately, and a complete description of each is given.

All film samples measured were gold deposited by thermal evaporation under reduced pressure. The reasons for choosing gold are as follows. Much of the experimental history includes research work on gold films. A large amount of data on the physical properties is known and published.[17] It was thought that some of these accumulated data might bear upon the interpretation of results. Gold has been used extensively as a shadow-casting material; therefore, measurements of the type described may be of value in controlled investigations in the field of electron microscopy. Since the techniques of evaporating gold are

---

[17] International Critical Tables of Numerical Data, Physics, Chemistry and Technology (The McGraw-Hill Book Co., Inc., New York, 1929).

well described and it is easily evaporated by heating under reduced pressure, it is a convenient metal to use.[18, 19] Gold, being rather inactive chemically, does not form the oxide when the film is exposed to air as has been indicated by the electron diffraction pictures by Germer.[20] The film structure remains constant with age which is an important factor if the films must be exposed to the atmosphere for some time before being measured. Some of the films were out of the evaporation chamber for as long as an hour before they were measured.

In addition to the reasons listed above, gold was chosen because of its adaptability to the radioactive tracer method used in this experiment. Au^{198} can be produced in a pile by bombarding natural gold, Au^{197}, with fast neutrons.[21] This means that a quantity of natural gold is bombarded until sufficient atoms have become radioactive to produce a sample that can be easily traced throughout an experiment. The chemical and physical properties which are significant in

---

[18] W. C. Caldwell, J. App. Phys. 12, 779 (1941).

[19] L. O. Olsen, C. S. Smith and E. C. Crittenden, Jr., J. App. Phys. 16, 425 (1945).

[20] L. H. Germer, Phys. Rev. 56, 58 (1939).

[21] E. McMillan and M. Kamen, Phys. Rev. 52, 375 (1937).

this experiment are the same for the Au^{197} and the product of bombardment, Au^{198}. This is important for it permits the entire sample received from the pile to be used without chemical separation. Of all other metals considered, no metal seemed to lend itself as well to this experiment as did the gold.

Preparation of Films by Evaporation

Since thermal evaporation under reduced pressure is becoming, more and more, the most popular method of depositing thin films and since many of the more recent investigators have used this method, it seemed the most likely method of deposition. Evaporated films contain less occluded and absorbed gases than those deposited by cathode sputtering. This is due to the outgasing of the source by heating to a temperature just below the sublimation or vaporization temperature preceding evaporation.[1] By measuring films containing less absorbed gas, the results should represent more nearly a measure of the true thickness.

All films were deposited on microscope slides having dimensions of 3 inches by 1 inch. These slides were sufficiently smooth over a very small area to satisfy the necessary interferometric conditions. In addition to this, being fire-polished, they did not introduce "fringe structure" in the interferometer fringes as did the polished,

optical flats. This is in agreement with the findings of Scott[22] in his work on film thickness measurements.

The films were deposited in a R. C. A. Vacuum Unit, type EMV-1A. The evacuation chamber consisted of a bell jar 18 inches in diameter and 29 inches in height. It was sealed to the base plate by means of a self-sealing rubber gasket which sealed under atmospheric pressure exerted on the outside. Six pairs of electrodes were built into the base plate. Each of these was capable of carrying 50 amperes to heat the filaments from which the coating substance was evaporated. There were two electrodes built into the base plate and connected to a high voltage transformer, which was capable of supplying voltage up to 7000 volts. This voltage was useful to ionize residual gases during the pump-down period before evaporation. The impact of the ions with the surface to be coated cleans the surface and makes for better adherence of coatings.[23] Also in the base plate was a cold cathode discharge gauge which was used to measure the chamber pressure. The fore pressure was measured by a thermocouple gauge.

The vacuum system consisted of a mechanical fore pump

---

[22] G. D. Scott, J. App. Phys. 21, 72 (1950).

[23] J. Strong, Procedures in Experimental Physics (Prentice-Hall, Inc., New York, 1938).

and a diffusion pump. The fore pump was a Cenco Hypervac 20. The diffusion pump was a vertical, water-cooled, oil pump filled with silicone fluid, DC-703. This system was capable of maintaining a kinetic vacuum at a pressure of 10^{-4}mm of mercury or better.

All glass microscope slides used as bases for the films were first thoroughly washed in a detergent, rinsed with hot distilled water and allowed to dry before being placed in the evaporation chamber. After cleaning, the slides were subsequently handled with lens paper to prevent contamination of the surfaces to be coated. During the evacuation of the chamber the glass slides were subjected to ionic bombardment in order to further clean the surfaces.

The gold was evaporated from small alumina crucibles prepared by fusing aluminum oxide on a small conical basket formed from 30-mil. tungsten wire. This proved very satisfactory since some of the gold evaporated was in lump form. A variation in sample thicknesses was obtained by placing the slides at different distances from the source. The minimum distance was about 20 cm. This minimum distance was maintained to insure uniform thickness, within experimental error, over a large enough area for subsequent comparison measurements. Since the deposition of the metal in the chamber follows very nearly the inverse square law, the variation of thickness from the center to the edge of an area 2 cm

in radius is only 10 A. U. for a film 1000 A. U. thick. This was about the accuracy obtained in the measurements.

Evaporation was completed in 20 to 40 seconds, depending on the film thickness desired, by supplying a filament current of about 15 to 20 amperes. This heated the crucible and sample until they were almost white hot. A temperature of about 2000°C to 2500°C was probably attained. Rapid deposition according to Sennett and Scott[14] produces more continuous films for a given thickness.

The method of obtaining comparable samples for both electron microscope and interferometer observations was as follows: Upon a microscope slide AC, figure 3, was placed a microscope cover slide B which was one half the length of the slide AC. With such an arrangement three useful samples, shown in figure 4, were produced. The samples A and C, figure 4, were obtained by cutting the glass slide AC along DE. The cover slide B, which was used as a shield for part of the base to produce a step in sample C, was an additional sample if needed. Sample A was measured by the shadow-casting method and sample C was measured with the interferometer. Since non-uniformities large enough to be measurable would exist if measurements were taken at the outer extremities of the slides, all data were taken on adjacent edges so that the maximum variation in thickness was below the accuracy of measuring.

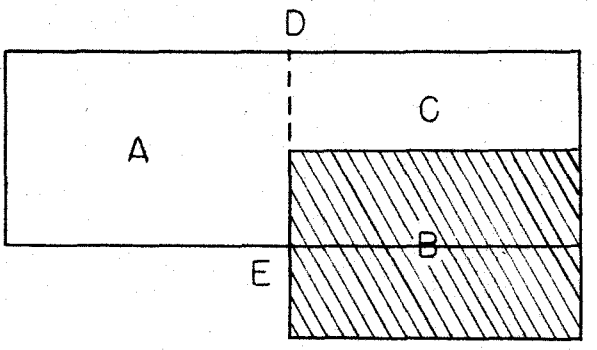

Fig. 3 Sampling arrangement of slides for shadow-casting and interferometric comparison.

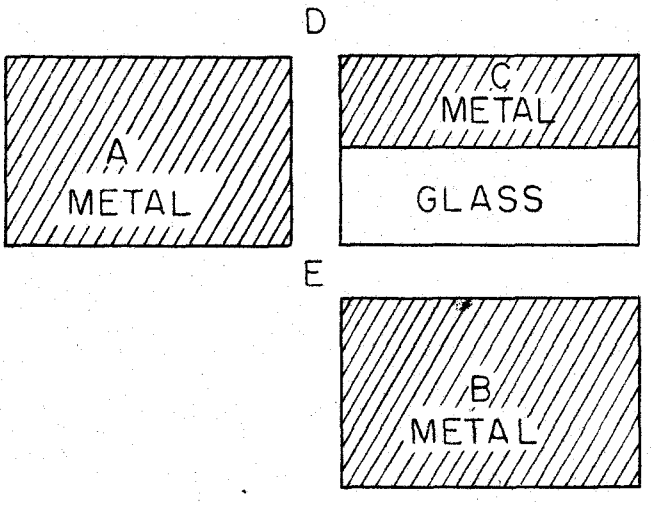

Fig. 4 Types of samples obtained by the arrangement of slides shown in Fig. 3.

The same sample was used for the comparison between the shadow-casting method and the interferometric method. It was necessary, however, to keep the area of the sample constant in order to reproduce the geometry of radioactive counting. This was done by covering one half of the microscope slide A, figure 5, with cover slide B during deposition. By repeating this on each sample, constant geometry was maintained. From such an arrangement, samples A and B, figure 6, were obtained. The activity from A was counted before the metal step DE, figure 6, was measured in the interferometer. Sample B was not used. The uncoated end C of the slide provided a means of handling the slide without damaging the coating.

Shadow-Casting Determination of Thickness

The coating on sample A, figure 4, was scratched with a sharp needle point or a razor blade. The scratching was done with just enough pressure to remove the metal from the glass but not enough pressure to scratch the glass. This formed a sharp scarp of metal over which the shadow-casting was done. A step formed by shadowing part of the slide during evaporation did not prove sharp enough to cast a shadow, but appeared as a gradual gradation from metal film to glass. Wiping the metal off with a tissue also failed to produce sharp discontinuities in the film.

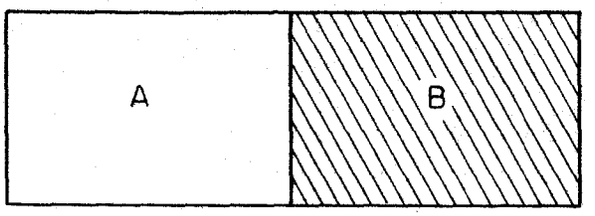

Fig. 5 Sampling arrangement of slides for radioactive and interferometric comparison.

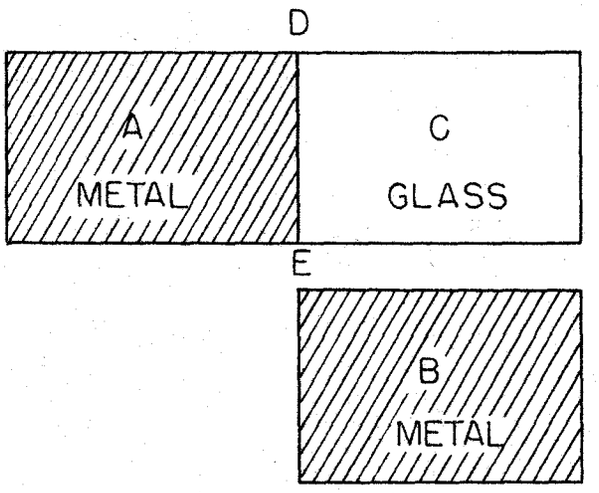

Fig. 6 Types of samples obtained by the arrangement of slides shown in Fig. 5.

After the film was scratched, it was shadow-cast in the same vacuum unit in which it was originally prepared. The sample was arranged so that the portion of the scratch to be used for measurements would have its shadow cast normal to the direction of the step. The shadowing was done at distances of 25 to 30 cm and arranged so that the shadows were five to six times longer than the film thickness. A rather large source-to-sample distance was maintained to increase the accuracy of measuring the angle of casting. The gold was evaporated from a very small, conical basket prepared of 10-mil tungsten wire. The area from which the gold was evaporated was kept small to increase the definition of the shadow boundary.

The shadow-casting was done at a pressure of about 2×10^{-4}mm of mercury. It was found that a good vacuum during evaporation produced sharper shadow boundaries. This is probably due to the increase of the mean free path of the evaporating metal; therefore, reducing the probability of scattering by gas molecules. The evaporation was done very rapidly, in a matter of a few seconds, in order to produce a more continuous film. As a result, the boundary definition was increased by the reduced agglomeration of the shadow-cast gold. The shadow coating was about 20 to 50 A. U. thick.

After shadow-casting, it was necessary to remove the metal film and the shadow coat from the glass slide to a

supporting base. This base must be relatively transparent to the electron beam of the microscope. It was first thought that the original metal film could be deposited directly on collodion or Formvar films, but no satisfactory method of producing a scarp without damaging the base or supporting film was found. It became necessary to make the transfer mentioned above.

A method of stripping replicas from surfaces such as glass is described by Schaefer[24]. He did this by drying a thin coat of collodion, diluted about ten to one with n-amyl acetate over the pre-shadow-casting, replica material, which may be a metal, and then stripping the whole off by means of scotch tape. This method was tried but was not found sufficiently dependable for this type of investigation. Many times the film did not strip successfully. At other times the film was stripped easily, but the shadow-casting gold would not come off with the sample.

The following method of removing the film and shadow from the glass on to collodion proved very dependable: A drop of diluted collodion (one drop of collodion to ten drops of n-amyl acetate) was placed on the slide and allowed to drain down over the scratch. It was then allowed to dry standing in a vertical position so that any excess collodion

---

[24]V. J. Schaefer, Phys. Rev. 62, 495 (1942).

could drain off. The thickness of the dried collodion film was such as to produce a bluish color with reflected white light. This thickness was rather critical since too thin a film had a tendency to stretch when in the electron beam of the microscope. If the collodion was too thick it obscured the edges of the film and shadows. By using as thick a collodion film as permissible and subjecting it to a low intensity beam in the microscope, stretching of the film was kept at a minimum. When the collodion was dry, the collodion, metal film and shadow were floated off on the surface of distilled water by introducing one end of the slide slowly into the water. It was found that this method of stripping the film from glass was successful without fail if a small drop of Octoil was placed on the crucible or basket from which the sample gold or shadow-casting gold was evaporated. This oil was heated to the vaporization temperature before the metal evaporated. This small amount of oil contamination evidently reduced the binding of the metal film to the glass.

After the transfer of the sample to the water surface, the microscope objective screens were dropped on the shadowed scarp. This was easily done since the scratch was visible. A microscope cover slide was dropped on top of the screens and the whole picked up from the surface of the water on the slide. A solution containing polystyrene latex

spheres, lot #3584, obtained from the Dow Chemical Co., was then sprayed on the sample to furnish internal calibration or a measuring reference.[25, 26] When the samples had dried sufficiently, they were ready for the electron microscope.

An R. C. A. Type EMU Electron Microscope was used to observe and photograph the samples. This scope has a resolving power of about 30 A. U. The photographs were taken on Eastman Kodak medium contrast lantern slides. These slides have a resolution of 70 lines/mm. This means that a magnification of at least 4760 diameters will record 30-A. U. detail on the photographic emulsion. Since the resolving power of the eye is 0.1 mm, a further enlargement of at least ten times is necessary so that the 30-A. U. resolution of the scope can be utilized. This enlargement can be accomplished either photographically or by increasing the magnification of the microscope. If it is done photographically, very careful development of the film is necessary to reduce the grain size of the silver. If it is done by increasing the magnification of the microscope, the decrease of intensity increases the difficulty of focusing and increases the exposure time so that instabilities of the electrical circuit reduce the reliability of resolution. In this

---

[25] G. D. Scott, J. App. Phys. 20, 417 (1949).

[26] C. H. Gerould, J. App. Phys. 21, 183 (1950).

work a magnification of about 8500 diameters was used for photographing. These photographs were observed through an optical system with a magnification of 15 diameters. This gave an over-all magnification of about 120,000 diameters.

The lantern slides were developed for 3 minutes, at 68°F, in Eastman D-11 developer. This is a high contrast developer which increased the ease of making subsequent measurements. Samples of the photographs resulting from the above procedure are shown in figures 7 to 14 inclusive. These were negatively printed to make the shadows appear dark on a light background. The magnification of these photographs is about 25,000 diameters.

The length of the shadows and the diameter of the spheres were measured on an optical, linear comparator. The thickness t of the films in angstrom units was determined from the formula,

$$t = \frac{\text{shadow length}}{\text{sphere diameter}} \times \cot A \times 2590 \text{ A. U.}, \qquad (2)$$

where A is the angle of incidence of the shadow-casting material. The figure, 2590 A. U., is given as the diameter of the polystyrene latex spheres taken from measurements made by several different investigators.[26] The diameters of the spheres do not vary by more than 25 A. U.

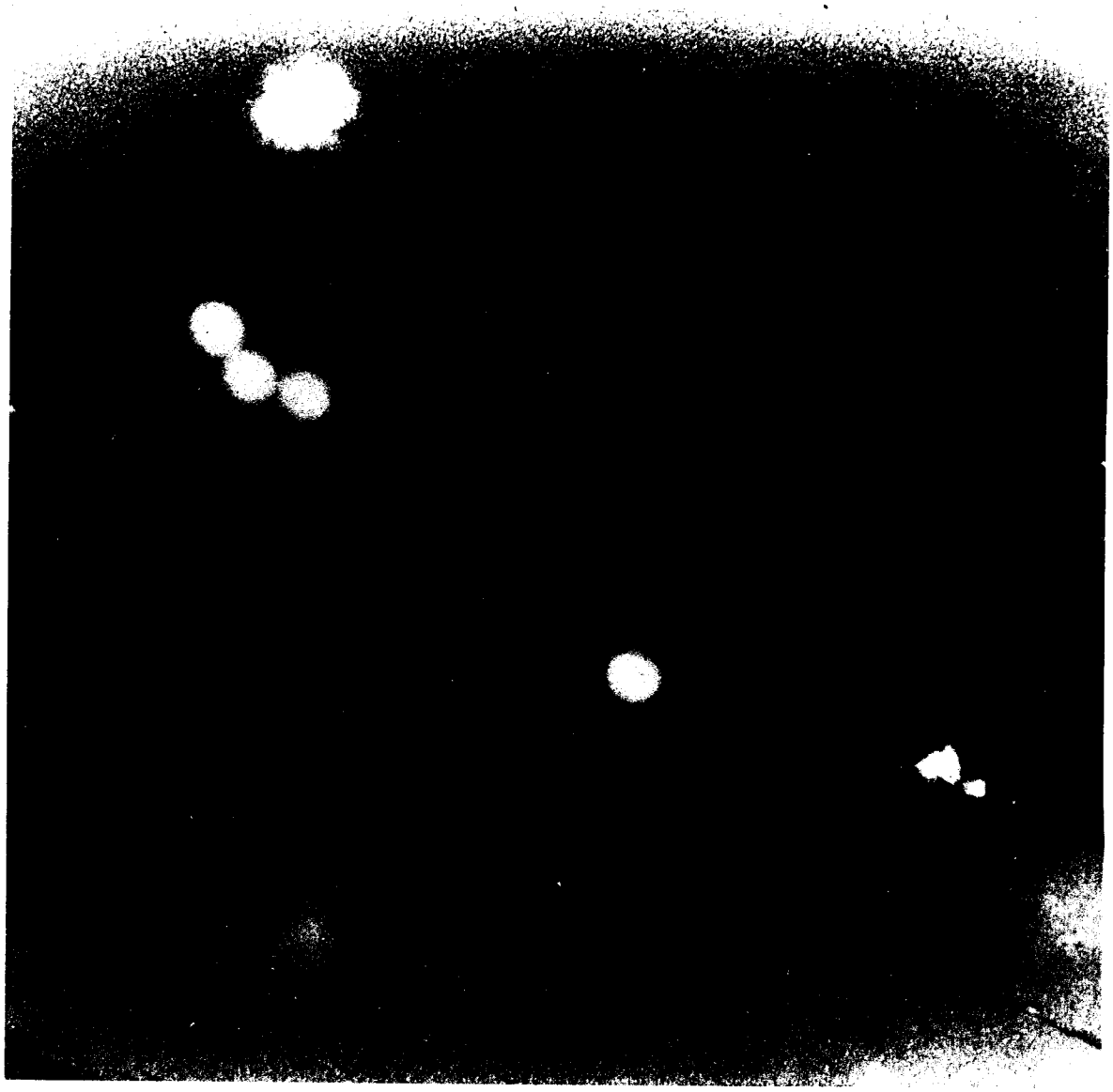

Fig. 7 Electron microphotograph of a gold-shadowed film 30 A. U. thick. The ratio of the shadow length to the film thickness is 6 to 1. The white spheres are polystyrene latex used for calibration.

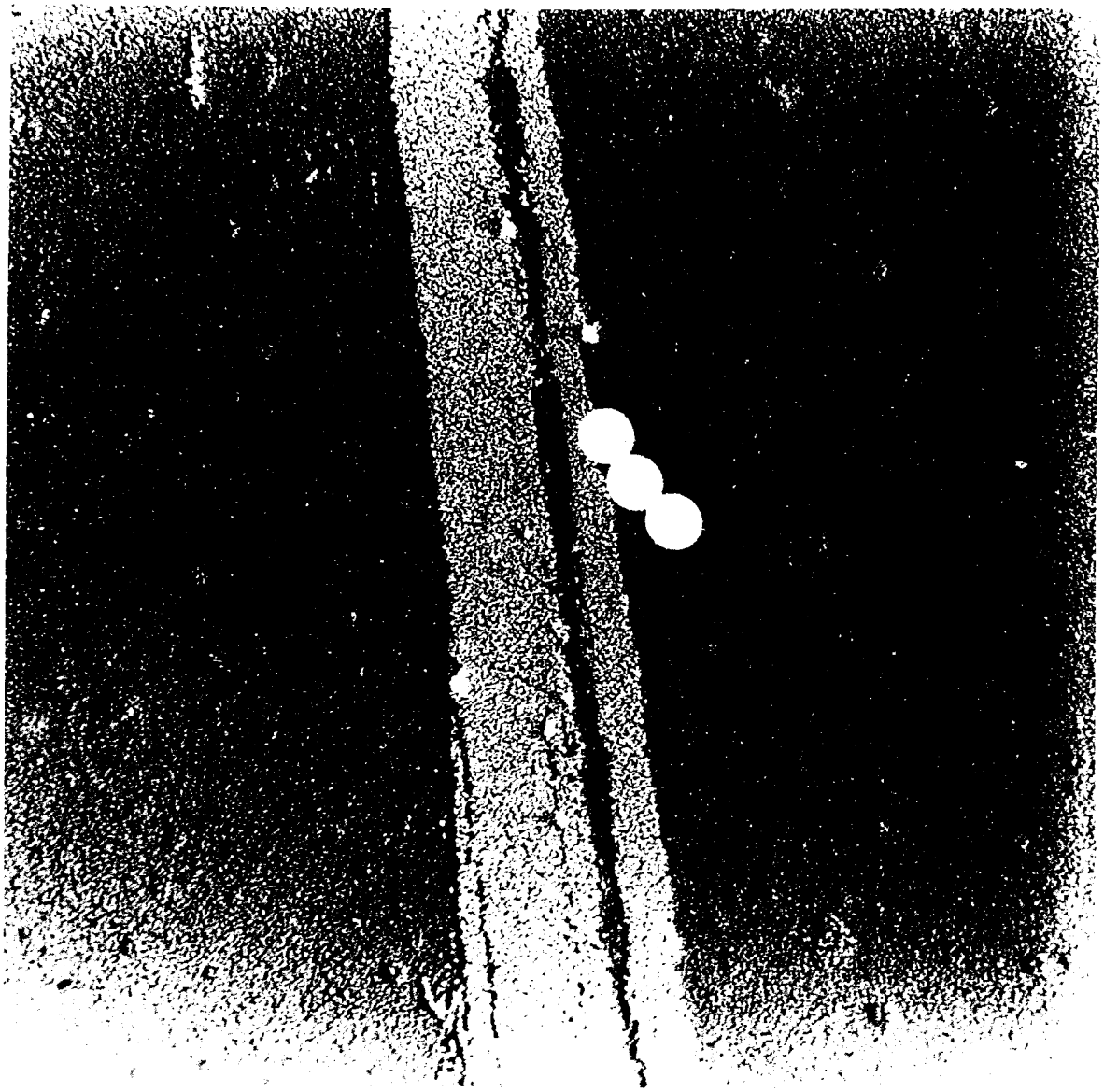

Fig. 8 Electron microphotograph of a gold-shadowed film 60 A. U. thick. The ratio of the shadow length to the film thickness is 21 to 4.

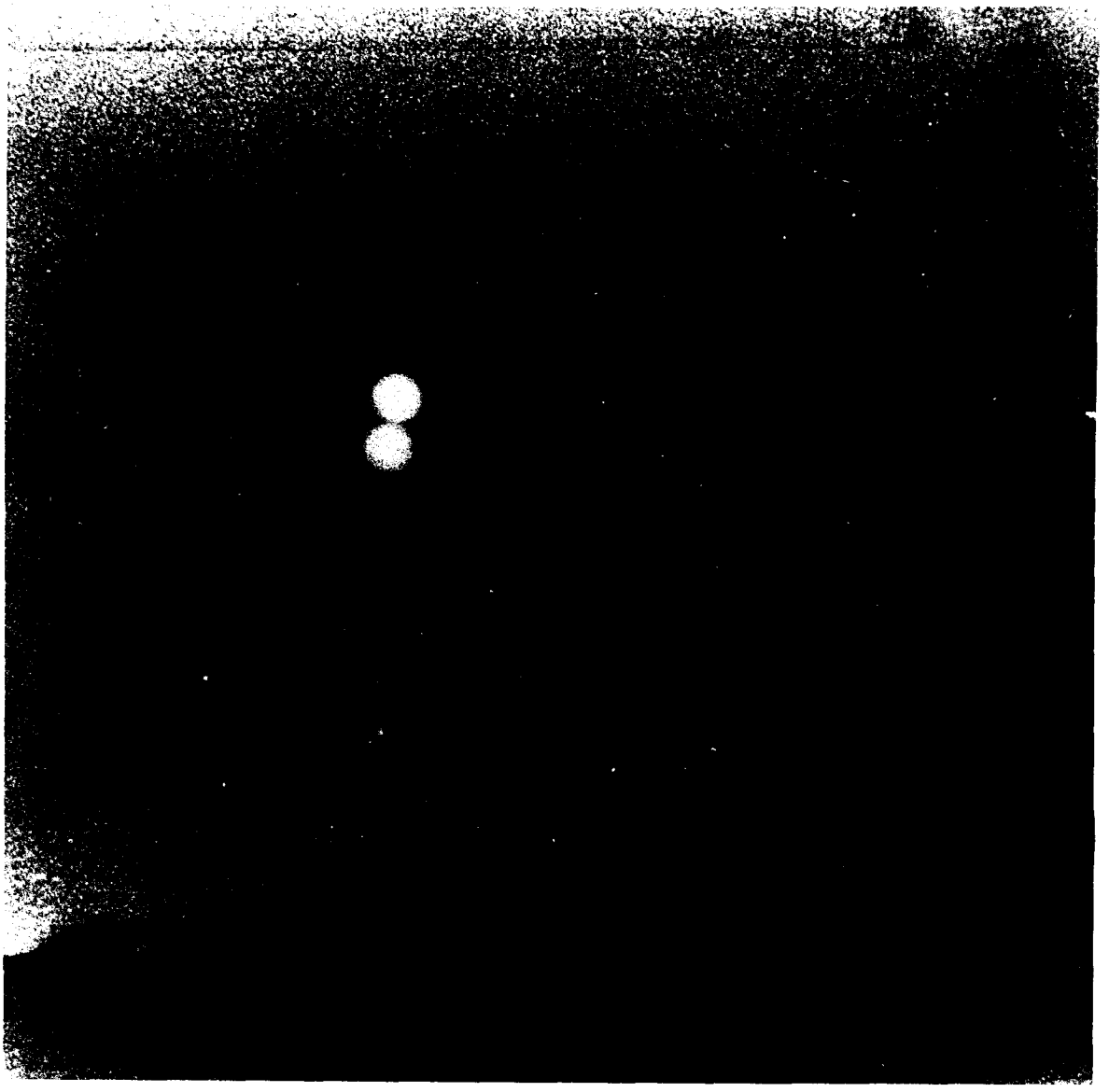

Fig. 9 Electron microphotograph of a gold-shadowed film 65 A. U. thick. The ratio of the shadow length to the film thickness is 27 to 5.

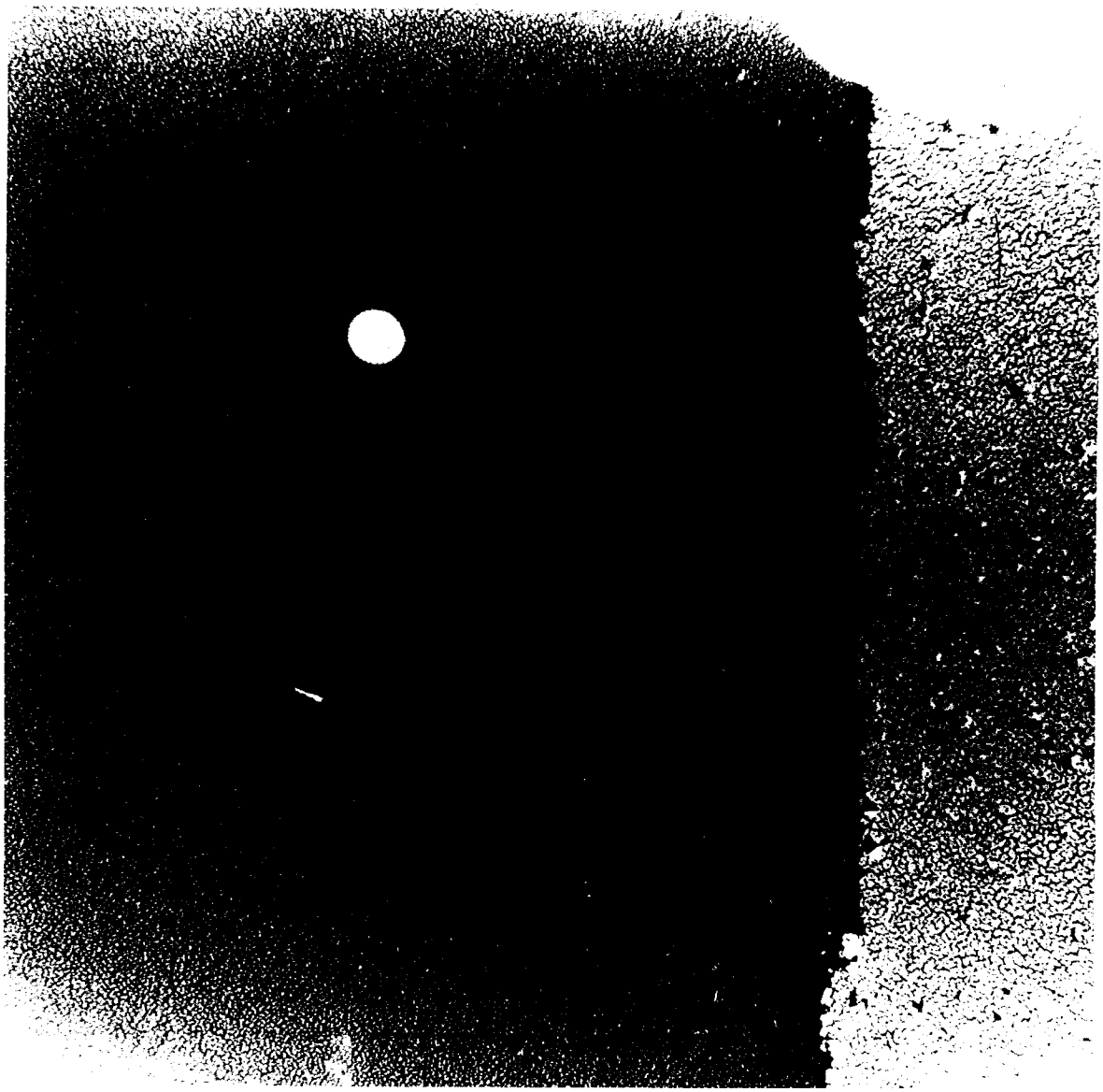

Fig. 10 Electron microphotograph of a gold-shadowed film 72 A. U. thick. The ratio of the shadow length to the film thickness is 27 to 5.

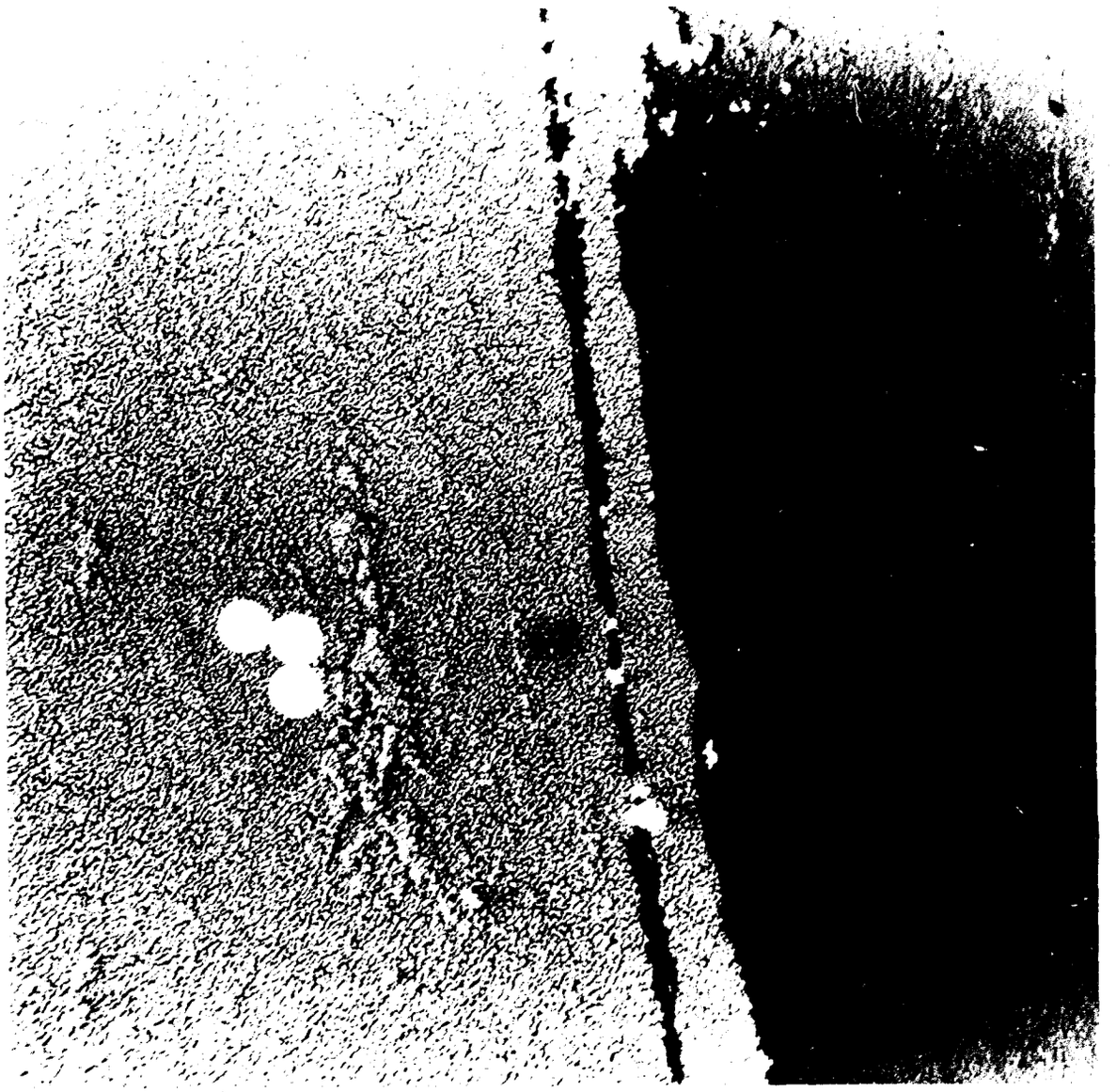

Fig. 11 Electron microphotograph of a gold-shadowed film 94 A. U. thick. The ratio of the shadow length to the film thickness is 26 to 5.

Fig. 12 Electron microphotograph of a gold-shadowed film 240 A. U. thick. The ratio of the shadow length to the film thickness is 27 to 5. The polystyrene latex spheres were shadowed, but the termini of the shadows are not easily located.

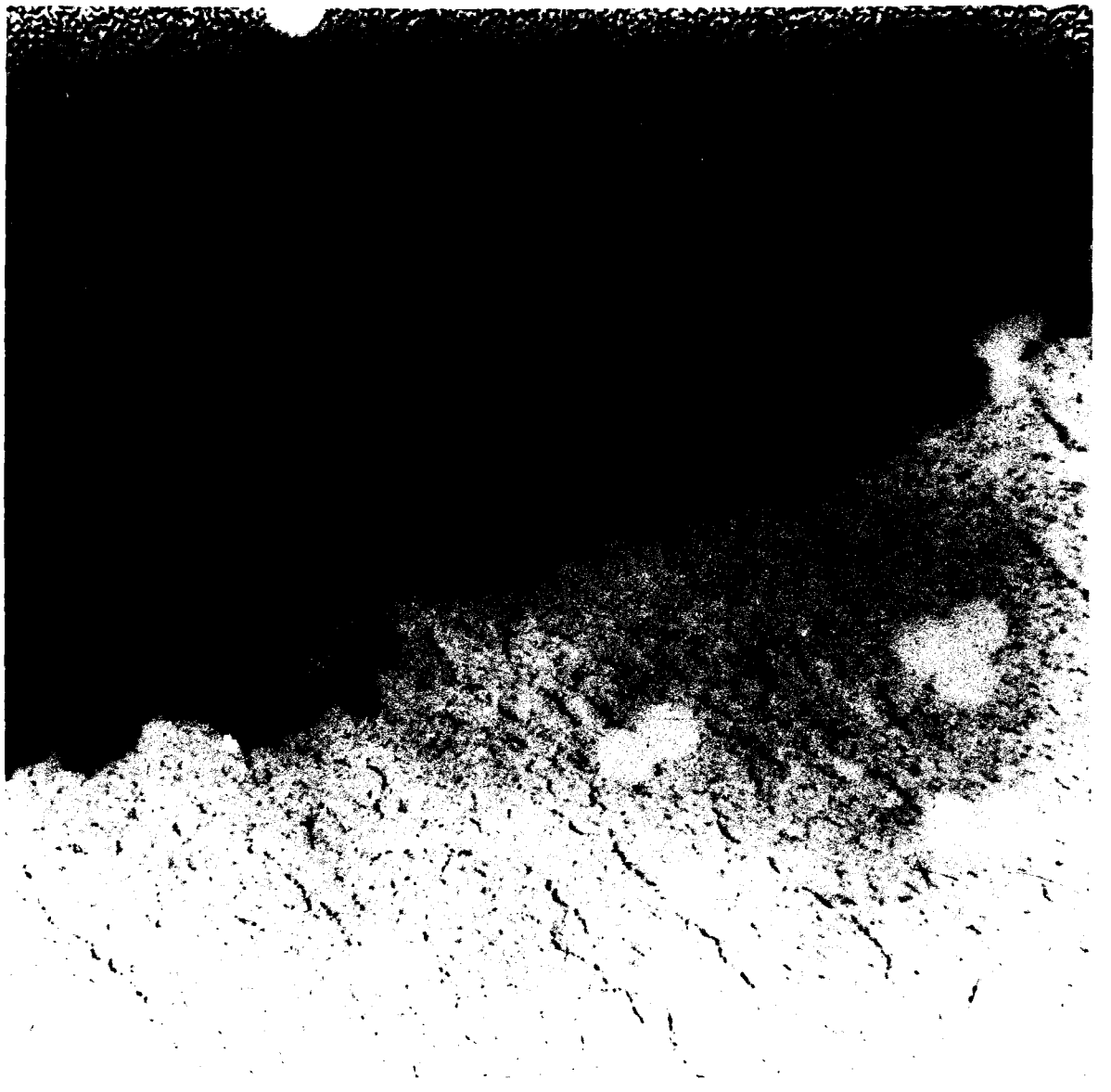

Fig. 13 Electron microphotograph of a gold-shadowed film 250 A. U. thick. The ratio of the shadow length to the film thickness is 5 to 1.

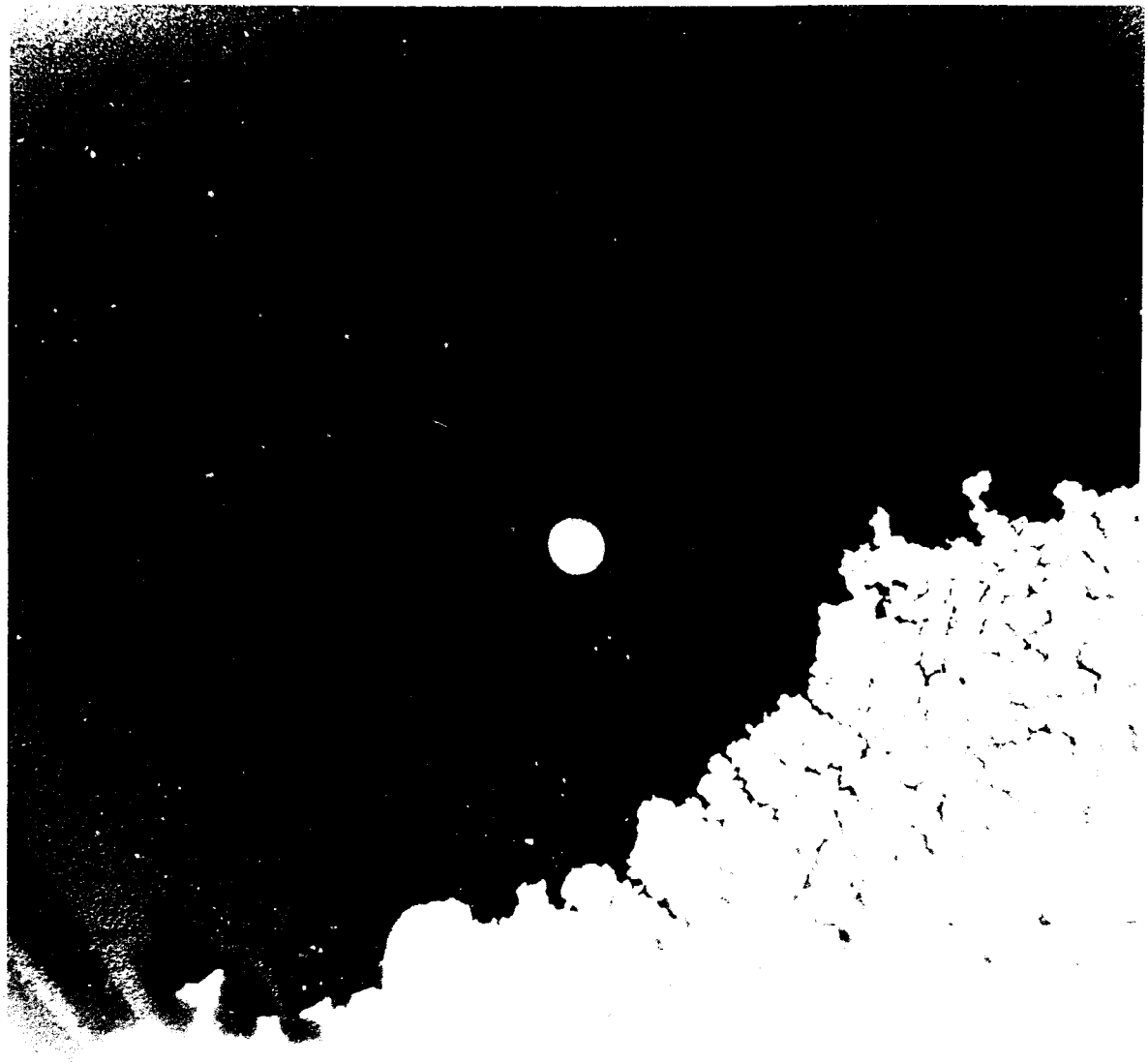

Fig. 14 Electron microphotograph of a gold-shadowed film 780 A. U. thick. The ratio of the shadow length to the film thickness is 27 to 5.

Interferometric Determination of Thickness

Sample C, figure 4, was used to make the interferometer measurements. The metal step was formed in most cases as described previously, but in addition, a step was formed by removing some of the metal by wiping it off with a soft point such as an orange stick. When a steel needle point was used, the glass base was scratched sufficiently to give an anomalous thickness measurement.

An opaque reflecting surface of silver was deposited over the entire face of the slide. The evaporation was done at less than 2×10^{-5} cm of mercury and deposited in a few seconds in order to produce a surface of high reflectivity and low absorption. The partially reflecting surface BC, figure 1, was prepared in the same manner. The transmission was measured during deposition by a phototube and light source placed within the vacuum chamber. Evaporation was continued until a transmission of about 5 percent was attained.

The optical arrangement shown diagramatically in figure 15 was used for the interferometer. This, as well as much of the other work in this section, was patterned after the methods of Tolansky.[27] S was the light source. A small

---

[27] S.Tolansky, Multiple-Beam Interferometry (Oxford University Press, London, 1948).

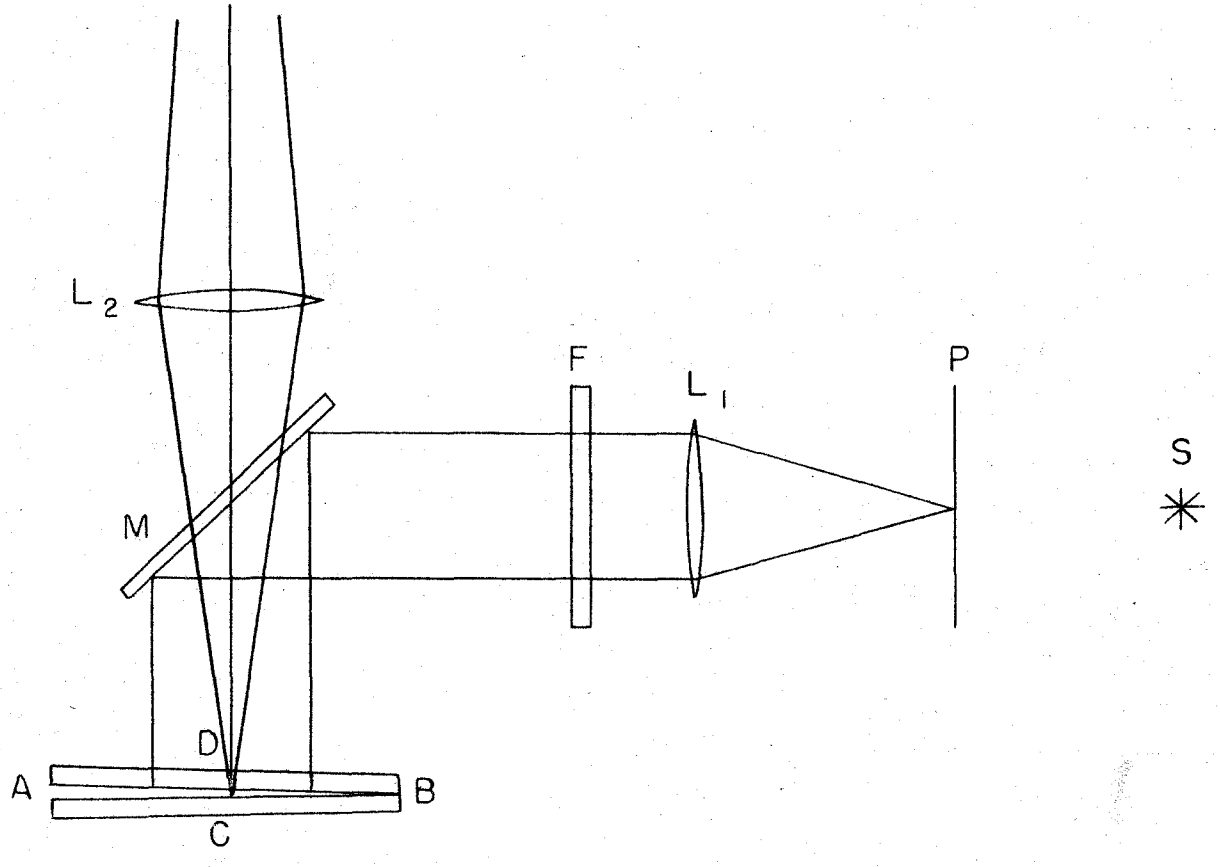

Fig. 15 Optical arrangement of the multiple-beam interferometer.

hole in screen P furnished a point source at the focal point of lens L_1. L_1 produced a collimated beam of light which was passed through the monochromatic filter. The parallel monochromatic rays were reflected from a half-silvered mirror M onto the interference plates C and D. The localized fringes formed by the interfaces of the interference plates were observed by focusing lens L_2 on the interfaces. L_2 was the objective lens of a low power microscope.

The interferometer arrangement used is shown photographically in figure 16. The source S was a high pressure, mercury vapor arc. L_1 was an f6.3 camera lens operated at full aperture. Screen P was a sheet of 1/16-inch steel plate with a 1.5-mm hole drilled in the middle. L_1 and P were housed in an ordinary view camera with P replacing the removable back of the camera. F was a liquid filter which consisted of a cuvette filled with a solution, 1 normal in $NdCl_6$, 0.025 normal in $K_2Cr_2O_7$ and excess HCl. This selectively transmitted the 5461 A. U. line of mercury with about one half the attenuation of the Wratten filters tried. C and D were the sample and the first interference plate shown in figure 1. In order to adjust the fringe pattern, it was necessary to place a small spacer in the form of a 1-mil wire between the plates C and D and apply a pressure at the four corners. This was done by means of the device shown in

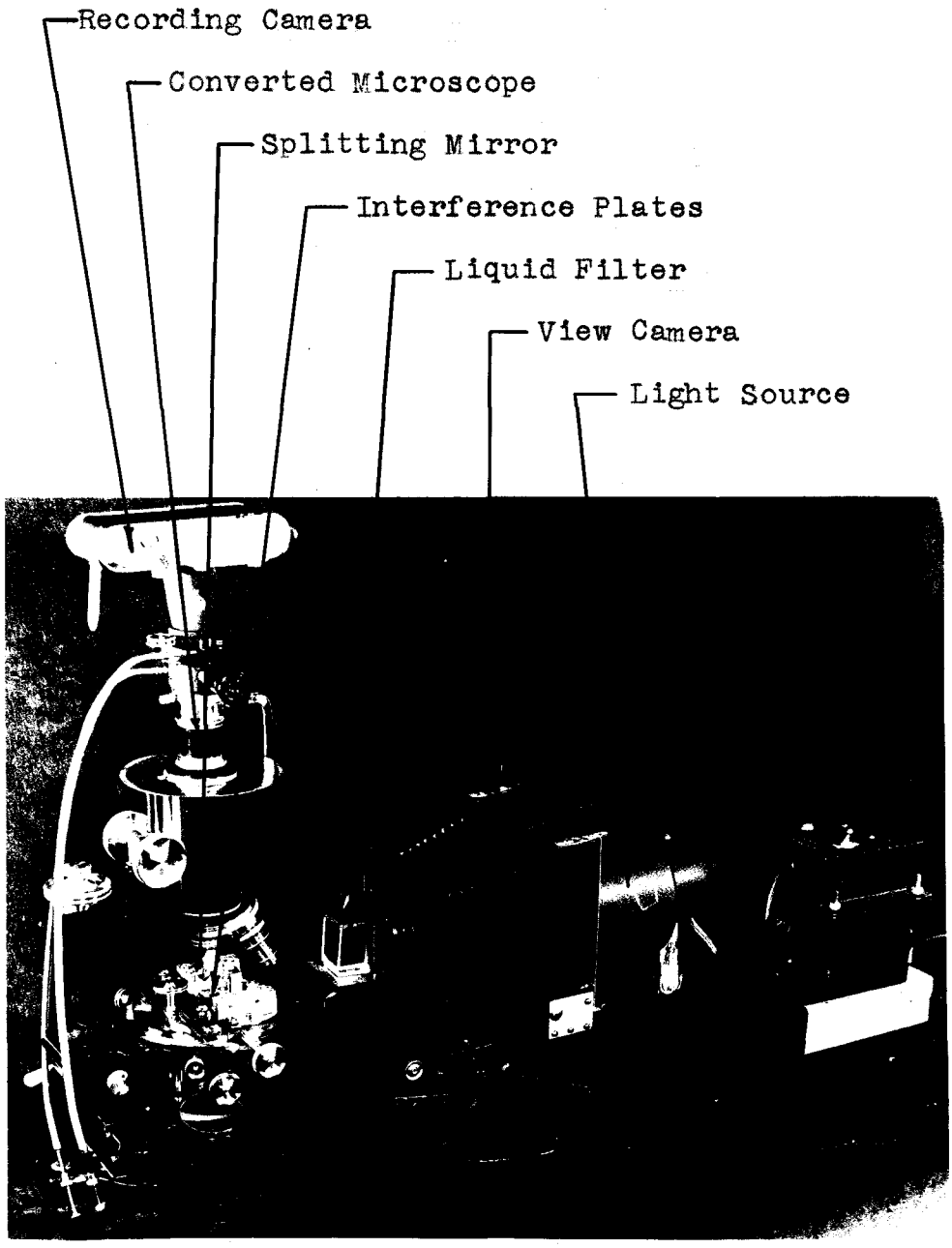

Fig. 16 Arrangement of multiple-beam interferometer.

figure 17. This carriage was placed on a movable microscope stage as shown in figure 18. An ordinary light microscope was used to observe the fringes. By removing one element of the low power objective lens, the focal length was changed from 16 mm to 32 mm. This allowed the half-silvered mirror shown in figure 17 to be assembled in place between the interference plates and the objective lens as shown in figure 18.

The fringe patterns were recorded on 35 mm Eastman linograph, orthochromatic film. The light intensity was sufficiently high so that an exposure of one minute gave very good pictures. The film was developed for four minutes in Eastman D-11 developer. This produced good contrast and increased the ease of measurement. Samples of the photographs obtained are shown in figures 19 and 20.

The fringe shift x and the fringe separation d, figure 2, were measured on an optical linear comparator. The film thickness was then calculated from equation (1).

Radioactive Tracer Determination of Thickness

The weighing of a small amount of metal deposited as a film was eliminated by introducing a radioactive tracer into the sample. By weighing a thick deposit, which could be weighed accurately, the weights of the thin samples were determined by a direct comparison of the counting rates. In order to do this the following precautions were necessary:

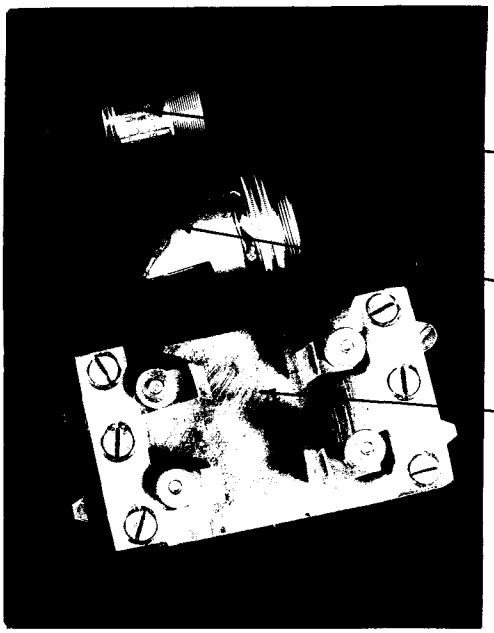

Fig. 17 Microscope-to-interferometer conversion parts.

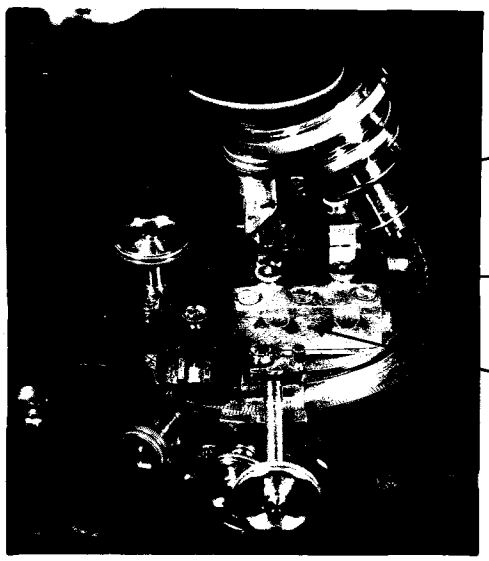

Fig. 18 Conversion parts assembled. The microscope stage can be rotated as well as translated.

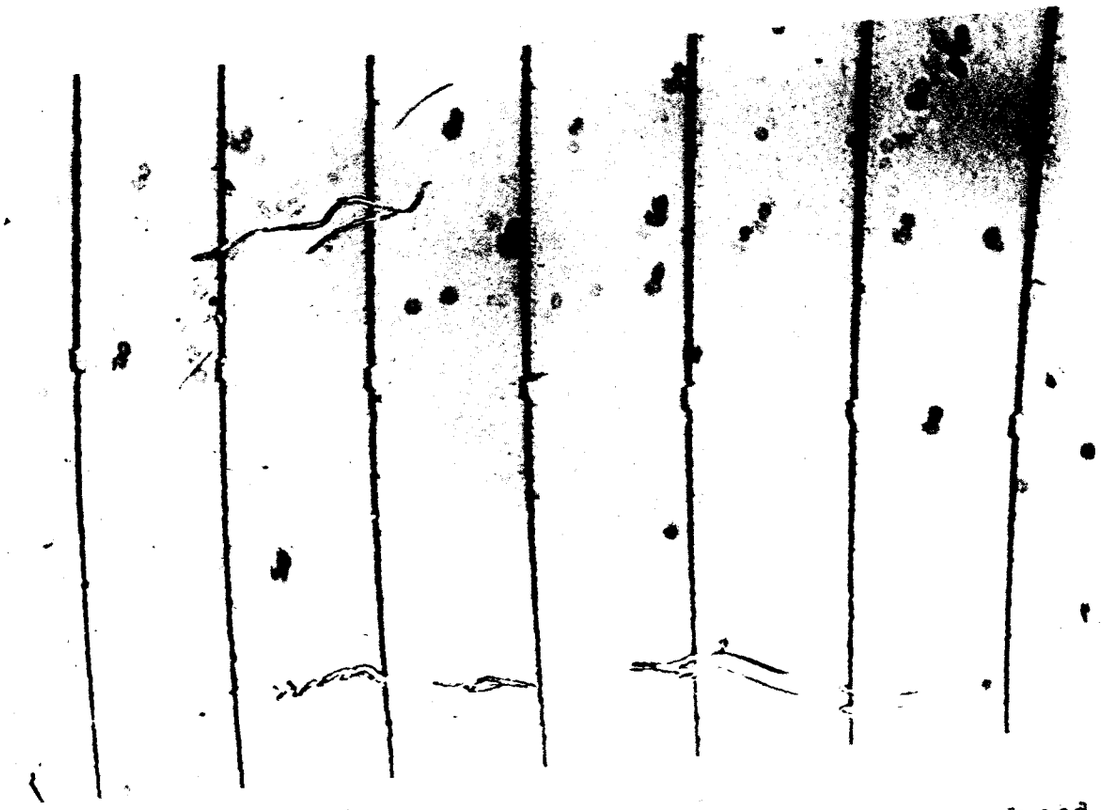

Fig. 19 Interference fringes showing the shift produced by a metal film 43 A. U. thick. The fringe spacing corresponds to 5641 A. U.

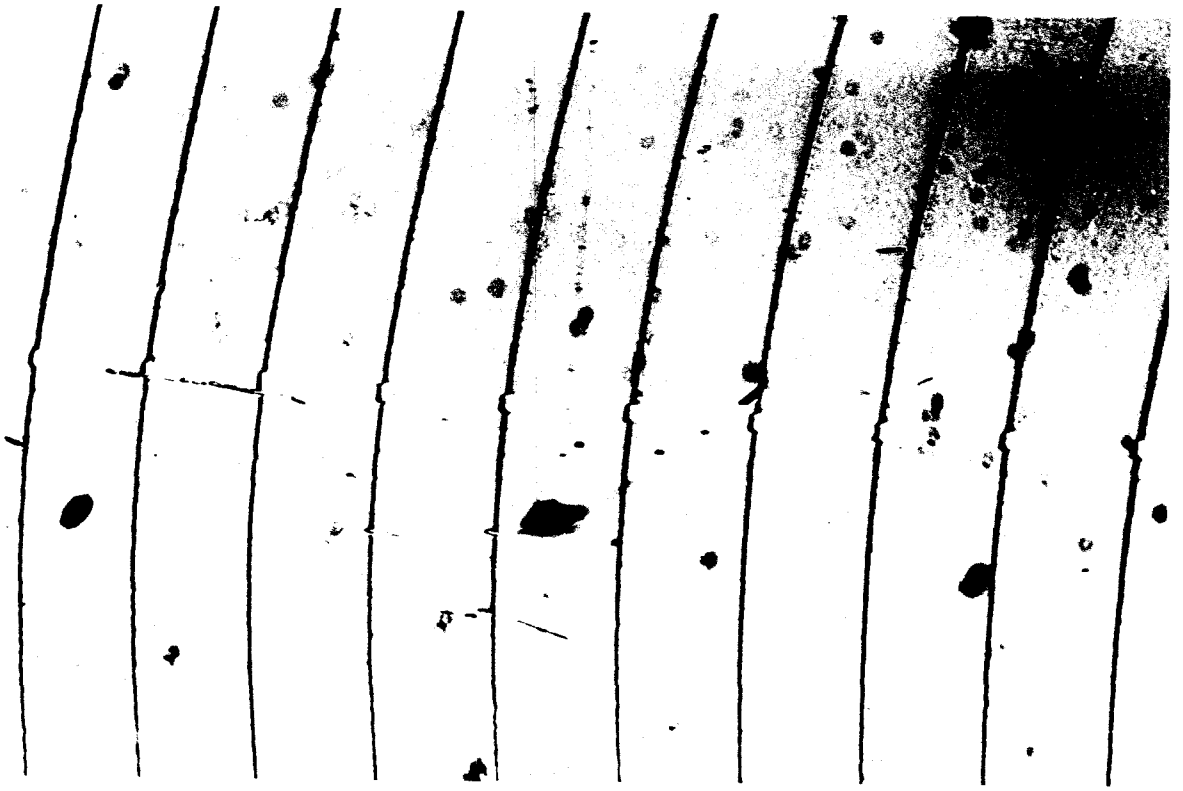

Fig. 20 Interference fringes showing the shift produced by a metal film 53 A. U. thick. The fringe spacing corresponds to 5641 A. U.

(1) The areas of all samples were constant, including the reference sample; (2) the same geometry of counting was maintained throughout; (3) the same detection device was used throughout; and (4) any anomalous effects on counting were eliminated or corrected if they were a function of the thickness.

The constant areas were maintained by the method described previously. The reference sample was a heavily deposited film of the same type as the other samples measured. The weight of the deposited metal was determined by weight differences, before and after deposition. Assuming a bulk density for the film, the thickness of the sample was accurate to $\pm$10 A. U. This was approximately the accuracy attained by the other methods. The total mass measurement was corrected to a thickness measurement at the step DE, figure 6. This was accomplished by assuming an inverse square distribution for evaporation of the metal from the source, then applying the formula derived in the following paragraph.

The mass per unit area D of the film deposited on the area dydx, figure 21, at a distance l from the source is

$$D = \frac{k}{l^2} \cos\phi, \qquad (3)$$

where k is a constant of proportionality. The cosine of the angle ϕ can be expressed as

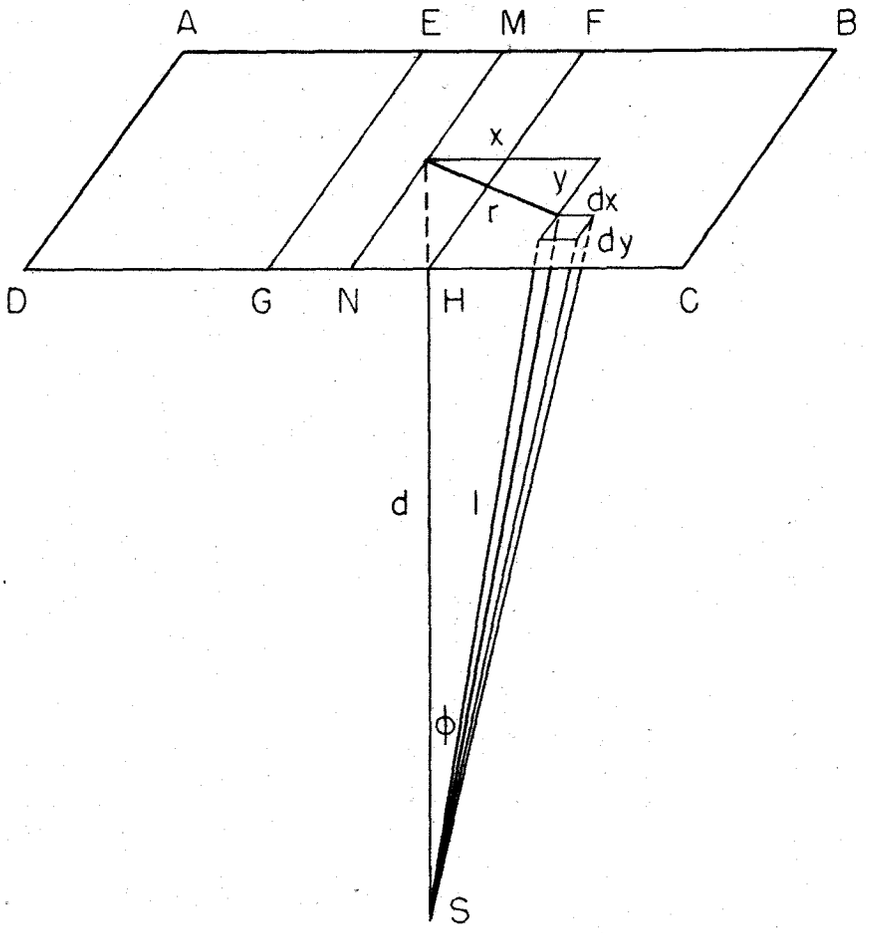

Fig. 21 Geometry of evaporating metal from a point source to a rectangular plane.

$$\cos \phi = \frac{d}{l} = \frac{d}{(r^2 + d^2)^{\frac{1}{2}}}, \qquad (4)$$

but

$$r^2 = x^2 + y^2. \qquad (5)$$

Therefore, the mass per unit area of metal on the area dxdy is given by

$$D = k \frac{d}{(x^2 + y^2 + d^2)^{3/2}}. \qquad (6)$$

The total mass M deposited over the area NMBC is

$$M = AD = 2 \int_0^b \int_0^a dxdy \frac{kd}{(x^2 + y^2 + d^2)^{3/2}}, \qquad (7)$$

where A is the area, a is the distance from the center of the slide to the edge BC and b is the distance from the center to the edge CD. By integrating equation (7), the following expression for the total mass is obtained:

$$M = \frac{K}{d} \tan^{-1} \frac{ab}{d(a^2 + b^2 + d^2)^{1/2}}. \qquad (8)$$

K contains all the numerical and proportionality constants. If the mass M deposited on the area NMBC is known, the mass M_1 deposited on the area MNFH can be calculated from the following ratio:

$$\frac{M_1}{M} = \frac{\tan^{-1} \frac{a_1 b_1}{d(a_1^2 + b_1^2 + d^2)^{\frac{1}{2}}}}{\tan^{-1} \frac{ab}{d(a^2 + b^2 + d^2)^{\frac{1}{2}}}}, \qquad (9)$$

where a_1 is the distance from the center of slide to the line FH and b_1 is the distance from the center to the edge CD. The area MNFH was chosen small enough so that the variation of thickness from the edge FH to the center MN was less than the experimental accuracy of 10 A. U. This varied with the distance d from the source.

Constant geometry was maintained during all the counting by fixing the Geiger tube in position and placing all samples at a fixed position on a shelf below the tube. The counting system consisted of a Radiation Counter Laboratory G-M tube, Model III, Mark 1, working into a standard scaler and mechanical counter. By using the same Geiger tube throughout, any irregularities, such as tube efficiency, etc., were eliminated.

The absorption of back-scattered radiation by the sample and self-absorption of radiation originating below the surface of the sample produce a secondary effect upon the counting rate. This alters the linear relationship between thickness and counting rate. This effect is important in the case of low energy beta emission where the absorption coefficient is high, but for high energy beta and penetrating gamma radiation it can be neglected.

Au^{198} disintegrates by the emission of a 0.960 Mev beta or by a beta of less energy followed by low energy

gamma rays both of which are followed by a 0.4 Mev gamma ray.[28] The low energy beta rays were shielded from the counter by a thickness of Al between the sample and counter window. By counting only the gamma rays and high energy betas, the anomalous effects on counting rates discussed above were eliminated.

The radioactive gold was obtained through the A. E. C. from the Oak Ridge pile. A 16-mg sample with an activity of 50 millicuries was received. Pure Au^{198} with a half-life of 2.7 days[28] has a specific activity of more than 10^5 times the specific activity of the sample received; therefore, the sample was less than 1 part of Au^{198} to 10^5 parts of natural gold. This means the disintegration product, Hg, was not present in sufficient quantity to be considered a contaminant.

It was desirable to have a larger sample to evaporate so that the deposition could be done at some distance from the source in order to give more uniform films. Since even the thinnest films would give 50 to 100 times the counts necessary for accurate counting if formed of the 50-mc sample, it was possible to mix the radioactive sample with natural gold in a ratio of 1 to 50. To insure thorough mixing, it was done chemically. About 4 mg of the 50-mc

---

[28] G. T. Seaborg and I. Perlmann, Rev. Mod. Phys. 20, 585 (1948).

sample and 200 mg of natural gold were dissolved in about 5 ml of dilute aqua regia. This was evaporated to near dryness to reduce the concentration of nitric acid. More HCl was added and the solution again evaporated to near dryness. Enough water was added to give about 10 ml of solution. To this was added a saturated solution of hydrazine hydrochloride as a reducing agent. The gold precipitated out upon heating. The solution was centrifuged and the precipitate transferred to a crucible. The precipitated gold was in a rather bulky, sponge-like form. In order to reduce the bulk, it was heated to the melting point at which temperature it formed a bead of metal. This was then evaporated in the vacuum chamber to produce samples of the type shown in figure 6.

The thin samples were counted first before they decayed to a slow disintegration rate. Since the samples were counted consecutively, there was a time difference between the counting of samples. Because of the short half-life, it was necessary to correct all counting rates back to the time of counting of the first sample. After the samples were counted, they were prepared for interferometric measurements in the usual manner. The samples were allowed to stand for about three half-lives to allow the activity to decrease until they could be safely handled without shielding in the interferometric measurements.

EXPERIMENTAL RESULTS

A direct comparison was made of the thickness measurements of equivalent metal films deposited on glass substrate by evaporation in a vacuum. A tabulation of these data is shown in Tables I and II. In an experiment of this type, the time element prohibits the production of enough samples to give statistical results; therefore, the data were taken from the very best pictures produced.

The thickness measurements by the shadow-casting method represent a mean of ten to fifteen thickness measurements made along the length of any one scarp shown in figures 7 to 14 inclusive. Care was taken to choose that part of the scarp which represents the true thickness of the metal and not an irregularity such as a fold. The variation of the measurements along the length of the scarp was always less than 10 A. U.

The thickness measurements by the interferometric method represent a mean of the thickness measurements from four or five fringe shifts along the step. Care was taken to choose those fringes which were uniform, straight and normal to the step. Again the largest variation in measurements on a given sample was less than 10 A. U.

In obtaining the data by radioactive counting, a sufficient number of counts were taken for each sample to give a probable error of less than one percent. The standard sample from which the weights of the thinner samples were determined by comparison of disintegration rates was weighed accurately to ± 0.5 percent. The thickness measurements by this method were reproducible to within 5 A. U.

A comparison was then made between the measurement of thickness obtained with interferometer on each film and the measurement of thickness obtained by the shadow-casting method applied to each companion film. The results of this comparison appear in Table I.

Table I. Comparison of thickness measurements by shadow-casting and interferometric methods.

Sample number	Film thickness by		Difference (S.C. - Int.)
	Shadow-casting	Interferometer	
1	30 A. U.	28 A. U.	2 A. U.
2	48	42	6
3	50	46	4
4	51	43	8
5	57	53	4
6	62	56	6
7	63	60	3
8	80	73	7
9	82	78	4
10	103	83	20
11	107	87	20
12	125	98	17
13	222	180	42
14	285	242	43
15	286	250	36
16	544	450	94
17	657	560	97
18	780	675	105

A curve of the results presented in Table I is plotted in figure 22. No attempt was made to fit the curve to the points, but instead, a straight line was drawn to show the general trend of the curve. None of the points lie off this straight line more than 10 A. U. The dotted line indicates a one-to-one ratio of the thicknesses measured by the two methods.

A second comparison was made between the measurement of thickness obtained with the interferometer on each film and the measurement of thickness obtained by the tracer method applied to the same film. The results of this comparison appear in Table II.

Table II. Comparison of thickness measurements by radioactive tracer and interferometric methods.

Sample number	Film thickness by		Difference
	Radioactive tracer	Interferometer	(R.T. - Int.)
1	45 A. U.	53 A. U.	- 8 A. U.
2	53	57	- 4
3	85	98	-13
4	114	126	-12
5	152	165	-13
6	152	161	- 9
7	154	171	- 8
8	201	212	-11
9	209	225	-17
10	340	321	19
11	367	335	32
12	410	375	35
13	430	390	40
14	462	423	39
15	617	565	52

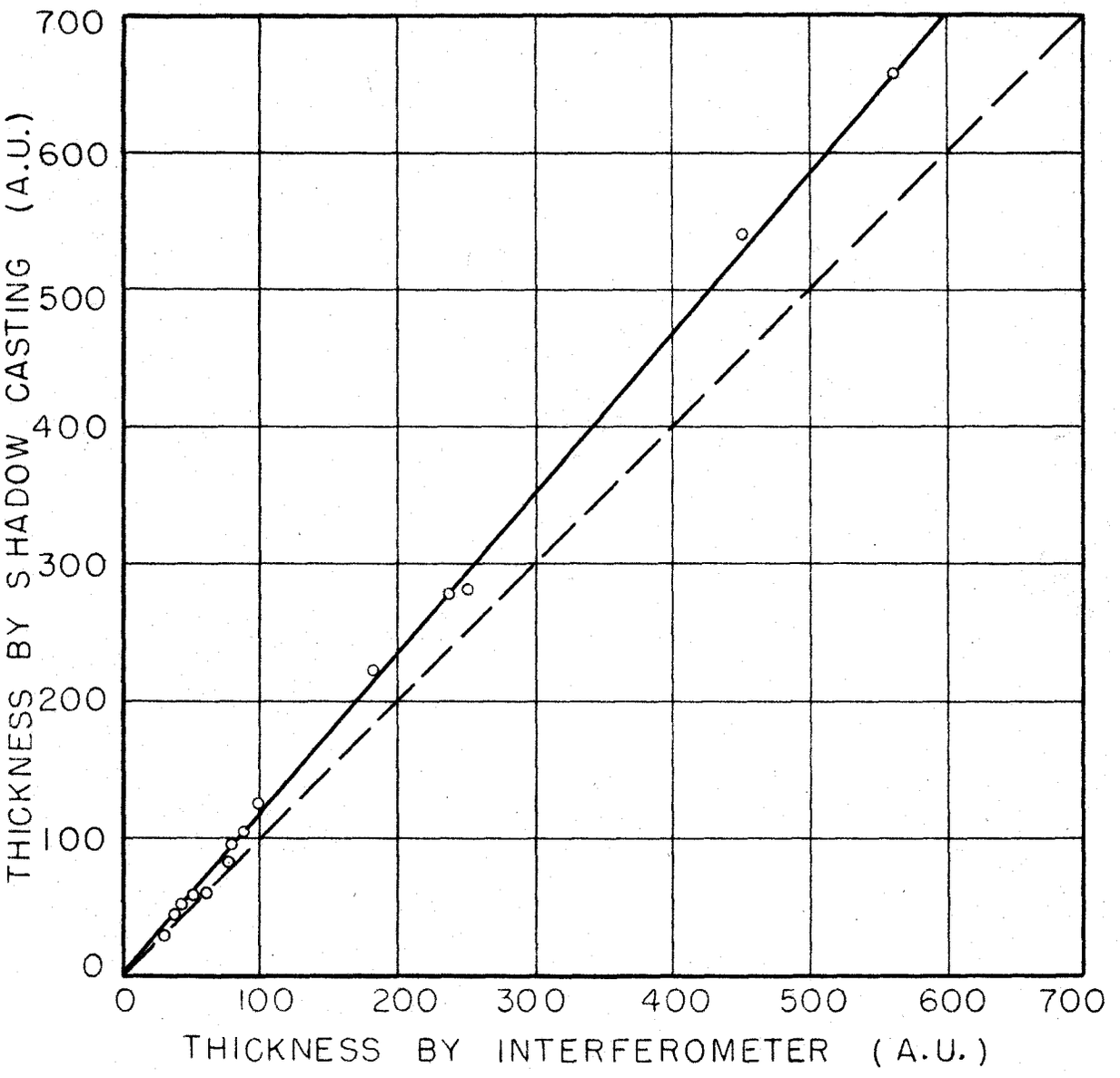

Fig. 22 Comparison of thickness measurements obtained by shadow-casting and interferometric methods of measuring thin-film thicknesses.

A curve of the results presented in Table II is plotted in figure 23. Again the general trend of the curve is indicated by a line drawn to include most of the points. Since no points fell close to the cross-over point of the two curves in figure 23, that portion of the curve was dotted to indicate a possible method of connecting the upper and lower parts of the curve.

Since the shadow-casting method appeared to give no anomalous thickness measurements, the other two methods were directly compared with it. To make this composite comparison, the curves shown in figure 24 were transposed from figures 22 and 23.

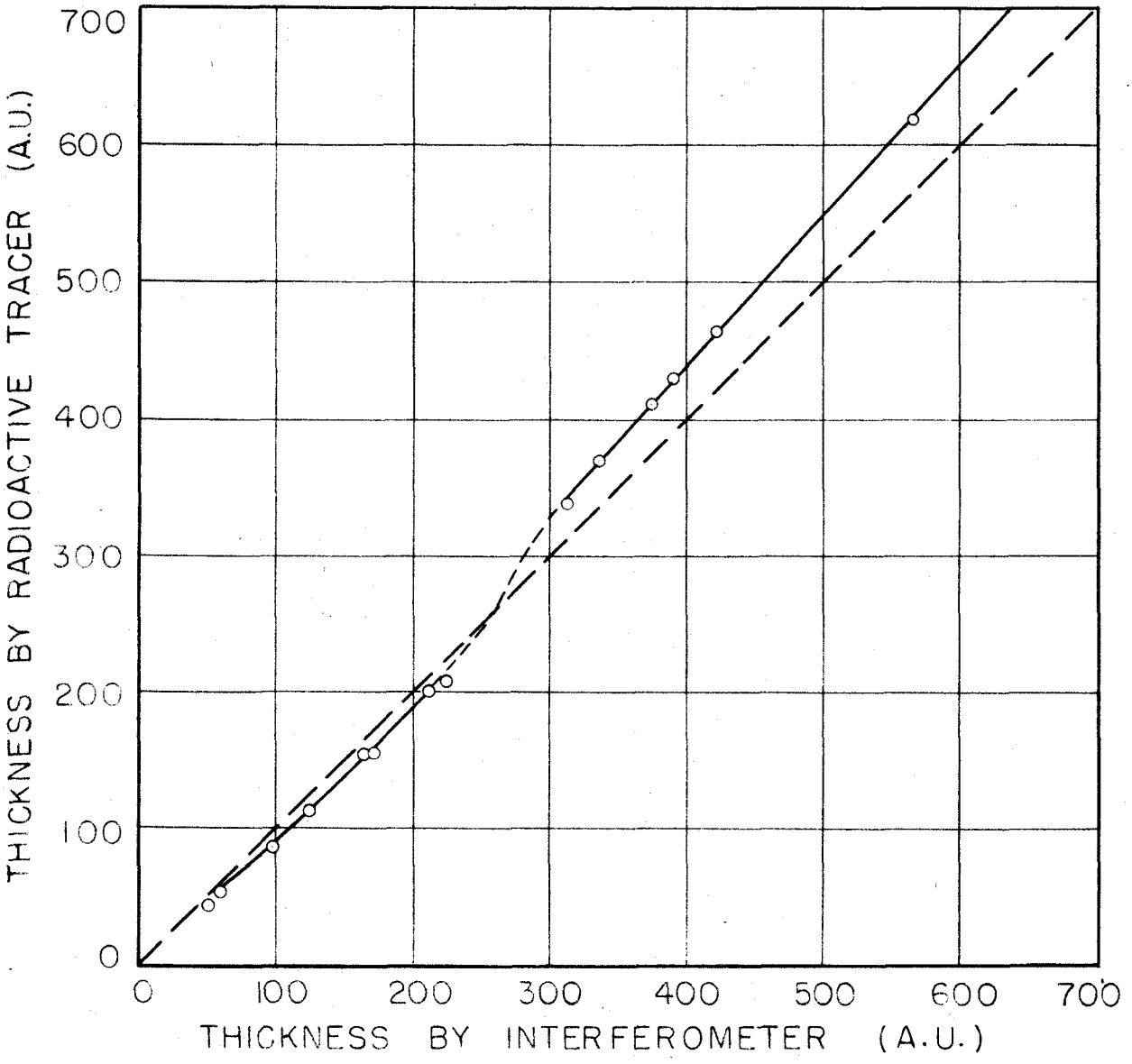

Fig. 23 Comparison of thickness measurements obtained by radioactive tracer and interferometric methods of measuring thin-film thicknesses.

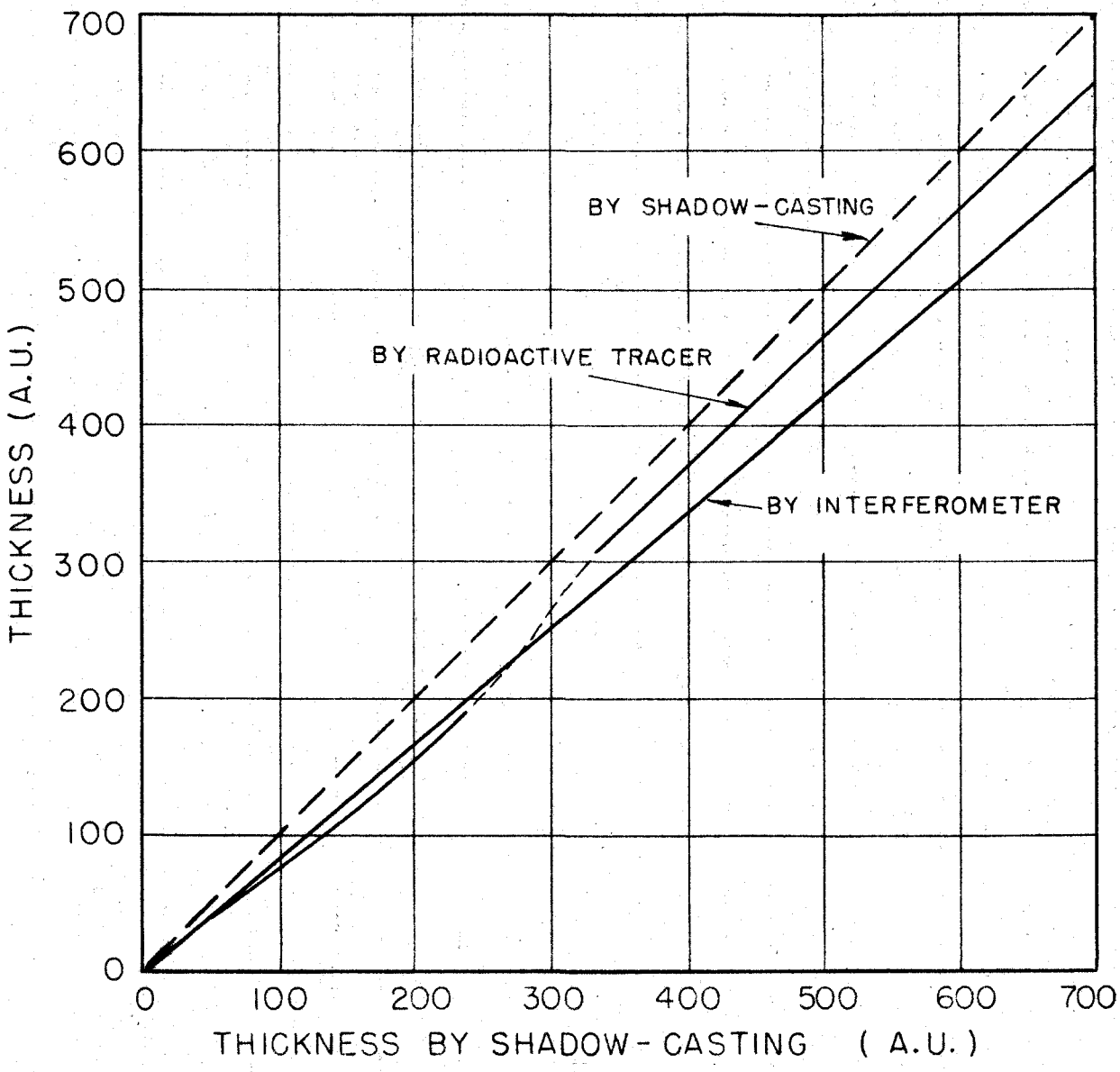

Fig. 24 A composite comparison of the interferometric, radioactive tracer, and shadow-casting methods of measuring thin-film thicknesses.

DISCUSSION

The purpose of this investigation was to study the reliability of each method of thickness determination and to make a direct comparison of the three methods to see if each method measures the same physical quantity.

The reliability of the shadow-casting method is best demonstrated by the reproducibility of readings on a given film and by the magnitude of the largest average deviation of film-thickness readings along the scarp. Readings could be reproduced at a given point on the scarp to within 5 A. U. The variation in film-thickness measurements along the scarp did not exceed 10 A. U.

The interferometric method proved equally reliable. The measurements in a single fringe shift were reproducible to less than 5 A. U. The variation in film-thickness measurements along four or five fringe shifts did not exceed 10 A. U.

A comparison of the two methods shows a systematic deviation with the shadow-casting method indicating a greater thickness, which grows as the thickness of the film grows. This is further indication of the reliability of each of the two methods. Since the difference is proportional to the

thickness measurement, it shows that two diffrent quantities are being measured, one of which is proportional to the other.

In an attempt to account for this proportional difference in measurements obtained by the two methods, the following were considered: an incorrect value for the diameter of the polystyrene latex spheres used for calibration, expansion of the collodion films on which the shadows were observed, parallax during shadow formation, accuracy in measuring the angle of shadow casting, the build-up of shadow-casting metal forming the scarp and a "packing in" effect of the opaque silver coating used in the interferometric measurements. In the following paragraphs, each of these is considered separately.

The various methods of measuring the diameter of the polystyrene latex spheres give a maximum deviation of $\pm$ 25 A. U. This is approximately a one percent variation of the 2590-A. U. diameter and could produce a difference in measurement of one percent of the film thickness. For example, if the 2590-A. U. diameter were 25 A. U. too large, the thickness measurement of each shadow-cast film would be increased by only one percent. Therefore, this cannot account for the 15 to 20 percent difference in thickness measurements indicated in figure 22.

Thin collodion films used as specimen supports showed a tendency to expand when placed in the electron beam of the microscope. When the thickness of the collodion film was increased, this expanding appeared to decrease. By reducing the beam current of the microscope, the expansion was reduced. During this investigation the microscope was operated with very low beam current and the collodion films were as thick as permissible. The following check was made to determine the approximate amount of error due to expansion of the collodion film: Polystyrene spheres were placed on one sample and shadow cast at a known angle along with the metal scarp. The length of the shadows cast by the spheres were measured and were within 2 percent of the length calculated from the diameter of the spheres and the shadow-casting angle. Expansion of the supporting collodion film was ruled out as the possible source of the difference shown in figure 22.

The angle of shadow casting was measured accurately to within one percent. This would be a random type error which would not give rise to the unidirectional difference indicated in figure 22. The parallax which exists because of the finite size of the source from which the shadow-casting metal was evaporated could produce a maximum error of 2 percent in shadow length. Since this effect tends

always to reduce the shadow length, it would produce an error contradictory to the results obtained.

When a metal is cast over the scarp of a metal film, it is conceivable that the build up of the shadowing metal on the metal forming the scarp would produce a somewhat longer shadow than the film alone. Even if this is not the case, there is a possibility that a graduation of the shadow boundary is produced. This may cause the observer to psychologically place the boundary too far from the film edge. In either case, the increase of the shadow length should be constant for all film thicknesses since the same thickness of gold was cast on each sample. No such constant difference exceeding the errors of measurement existed. This is evidenced by the absence of a measurable intercept of the solid curve in figure 22.

Thomson[29] found that when metals are deposited on metals there is a strong tendency of the deposited metal to follow the lattice structure of the substrate metal if the crystal structure is not too different. The deposited metal fits into the vacancies of the substrate crystal structure rather than form its own crystals on the top of the substrate. This leads to a "packing-in" effect of the opaque

---

[29] G. P. Thomson, Proc. Phys. Soc. 61, 403 (1948).

reflecting layer of silver deposited over the gold film. Avery[16] found this effect present in the case of silver deposited on silver. He also found the effect to increase with an increase of the substrate thickness. This may be the cause for the observed difference in the measurements by the shadow-casting and interferometric methods. If this effect is present, it should reach a maximum at such thicknesses that the film takes on bulk aspects and should remain constant for greater thicknesses. It may also be possible to eliminate or at least reduce this effect by evaporating a layer of some material such as silica, which has a different crystal structure, over the entire surface of the sample before depositing the reflecting layer of silver. This would not affect the thickness measurements and would prevent intimate contact of like crystal structures. Further experiments in this direction should give some interesting results to confirm or nullify the proposal of a "packing in" effect.

A comparison of the radioactive tracer method with the shadow-casting method, shown in figure 24, shows a non-uniform variation for thicknesses less than about 350 A. U. This variation may be due to a variation in the density of the metal in the form of a thin film. In order to obtain the thickness from the mass, which was determined by comparing disintegration rates, it was necessary to assume a

constant density for the metal. The bulk density of the metal was used for all film thickness. Apparently this was too large throughout the thickness range measured. However, if the difference were one due only to density variation, the curve above 350 A. U. should approach the one-to-one curve asymptotically. Figure 24 shows a slight divergence of the two curves. No good explanation was found for this inconsistency. The self-absorption of the emitting sample would introduce an error in the proper direction to increase the slope of the tracer curve. However, the low energy beta radiation was shielded from the counter so that self-absorption in the range of thickness measured introduced a negligible error.

Discounting the variations just discussed, some factors which may be used to make a general evaluation of each of the methods are:

1. The shadow-casting method provides an electron microphotograph of the film. This may be of value in some cases.
2. The shadow-casting and interferometric methods both require a second deposition of metal, which increases the overall time of measuring.
3. The interference fringes obtained in the interferometric method can be measured directly by a traveling microscope, thus eliminating time

required for photographic recording necessary in the shadow-casting method.

4. The films measured by either the shadow-casting or interferometric method can not be used for further investigation since they are destroyed in the process of measuring the thickness.
5. The radioactive tracer method provides a convenient method of determining a very small amount of material deposited as a thin film without meticulous weighing of many samples. For thin films, the weight is determined more accurately than could be done by weighing the same sample. Tracers cannot be found for all materials.

SUMMARY AND CONCLUSIONS

A method for measuring the thicknesses of thin metal films by casting a metal over the edge of the films and observing the length of the shadows in the electron microscope was used. It consisted of depositing the film on glass substrate, producing a scarp of the film on the glass, shadow-casting the scarp with gold at a known angle of incidence, transferring the metal film and shadow to a collodion base on a microscope objective screen and observing the length of the shadows in the electron microscope.

A second method employed a radioactive tracer determination of the weight of metal deposited as a thin film over a known area; the thickness was then determined by assuming a bulk density for the deposited metal. The deposited gold was enriched with a small amount of Au^{198} before deposition. Sufficient active gold was added to give good statistics of counting in a relatively short time for the thinnest films. The weights of the thin samples were obtained by comparing the disintegration rates with that of an accurately weighed standard of much greater thickness. Constant counting parameters were maintained throughout, and care was taken to eliminate any error due to those that could not be kept constant. The weighing of

very small amounts of deposited metal was thus eliminated while the accuracy of determination was increased over that of weighing of the same samples.

The thickness of each film or its equivalent measured by either of the two methods described above was also measured by the Tolansky interference method. By so doing, a direct comparison of the three methods was accomplished. As a result of this comparison, the following conclusions are drawn:

1. As outlined in this paper, the shadow-casting method of measuring the thicknesses of thin metal films is a reliable method in the thickness range of 20 to 1000 A. U., but needs some further development of techniques for thicknesses outside this range.
2. The Tolansky multiple-beam interferometric method of measuring the thicknesses of thin metal films measures consistently a physical quantity 15 to 20% less than that measured by the shadow-casting method. This measured quantity is the optical difference between two reflecting planes which are not separated by the thickness of the film being measured. The failure of the opaque reflecting layer of silver to follow completely the metal step can be attributed to a "packing in" effect of silver on the metal film. This effect increases with

increased thickness in the range of 20 to 1000 A. U.

3. The weight of metal deposited as a thin film can be determined by a radioactive tracer method, thus eliminating the meticulous weighing of very small quantities. The accuracy is also increased over that of weighing of the same sample.

This method of determining thickness fails to give a true thickness measurement since it is necessary to assume a constant density for the metal in the form of a thin film. If the density of thin metal films were known, this method provides a very accurate method of thickness determination.

LITERATURE CITED

Aron, P. A. Ann. Phys. Paris 1, 361 (1946).

Avery, D. G. Nature 163, 916 (1949).

Caldwell, W. C. J. App. Phys. 12, 779 (1941).

Friedman, H. Rev. Sci. Inst. 17, 99 (1946).

Germer, L. H. Phys. Rev. 56, 58 (1949).

Gerould, C. H. J. App. Phys. 21, 183 (1950).

Goos, F. Zeits. f. Physik. 100, 95 (1936).

-------- Zeits. f. Physik. 106, 606 (1937).

International Critical Tables of Numerical Data, Physics, Chemistry and Technology (The McGraw-Hill Book Co., Inc., New York, 1929).

Khamsavi, A. and Donaldson, W. K. Nature 159, 228 (1947).

McMillan, E. and Kamen, M. Phys. Rev. 52, 375 (1937).

Oldham, M. S. Ph.D. thesis, Department of Physics, I. S. C. (1949).

Olsen, L. O., Smith, C. S. and Crittenden, E. C., Jr. J. App. Phys. 16, 425 (1945).

Picard, R. G. and Duffenback, O. S. J. App. Phys. 14, 291 (1943).

Road, J. L. J. Opt. Soc. Am. 39, 854 (1949).

Schaefer, V. J. Phys. Rev. 62, 495 (1942).

Seaborg, G. T. and Perlmann, I. Rev. Mod. Phys. 20, 585 (1948).

Scott, G. D. J. App. Phys. 20, 417 (1949).

---------- J. App. Phys. 21, 72 (1950).

Sennett, R. S. and Scott, G. D. J. Opt. Soc. Am. 40, 203 (1950).

Strong, J. Procedures in Experimental Physics (Prentice-Hall, Inc., New York, 1938).

Thomson, G. P. Proc. Phys. Soc. 61, 403 (1948).

Tolansky, S. Phil. Mag. 35, 120 (1944).

---------- J. Sci. Inst. 22, 161 (1945).

---------- Proc. Roy. Soc. 184, 41 (1945).

---------- Proc. Roy. Soc. 186, 261 (1946).

---------- Multiple-Beam Interferometry (Oxford University Press, London, 1948).

Weale, R. Proc. Phys. Soc. 62, 576 (1949).

Williams, R. C. and Backus, R. C. J. App. Phys. 20, 98 (1949).

ACKNOWLEDGMENTS

The author is grateful to Dr. P. H. Carr under whose guidance this work was done and to Dr. Adolf F. Voigt whose cooperation contributed to the success of the radioactive measurements. Edgar H. Dewell was helpful with his contributions to the chemical phase of the work.

Grateful acknowledgment is also given to many others, who encouraged and cheerfully assisted the author.